

PATENT SPECIFICATION

(11) 1 467 098

1 467 098

(21) Application No. 26716/75 (22) Filed 24 June 1975.

(31) Convention Application No. 483 185

(32) Filed 25 June 1974 in

(33) United States of America (US)

(44) Complete Specification published 16 March 1977

(51) INT CL² C11D 10/00; (C11D 10/00, 1/00, 3/37)

(52) Index at acceptance

C5D 6A5C 6A5D2 6A5E 6B12A 6B12B1 6B12F1 6B12F2
6B12G2A 6B12G6 6B12N1 6B13 6C6

C3R 3C 3N2 C12 C13M C13S C21 C33B L2C1 L6H

(72) Inventors CHARLES H. NICOL and HUGH R. HAYS

(19)



(54) DETERGENT COMPOSITIONS HAVING IMPROVED SOIL RELEASE PROPERTIES

(71) We, THE PROCTER & GAMBLE COMPANY, a Corporation organised under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to particulate detergent compositions comprising a surface-active agent selected from anionic, nonionic, zwitterionic, and ampholytic surfactants, and mixtures thereof, and a particular type of soil-release polymer comprising ethylene terephthalate and polyethylene oxide terephthalate. The detergent compositions herein clean and can provide improved soil release benefits to synthetic fabrics, particularly polyester fabrics, as compared with known soil release agents employed in detergent compositions.

Much effort has been expended in designing various compounds capable of conferring soil-release properties to fabrics woven from polyester fibers. These fabrics are mostly co-polymers of ethylene glycol and terephthalic acid, and are sold under a number of tradenames, e.g., Dacron, Fortrel, Kodel (these three are trade marks) and Blue C Polyester. The hydrophobic character of polyester fabrics makes their laundering (particularly as regards oily soil and oil stains) difficult, principally due to the inherently low wettability of the polyester fibers. Since the character of the fiber itself is hydrophobic, or oleophilic, once an oily soil or oily stain is deposited on the fabric it tends to be "attached" to the surface of the fiber. As a result, the oily soil or stain is difficult to remove in an aqueous laundering process.

When hydrophilic fabrics such as cotton are soiled by oily stains or oily soil, it is well recognized that the oil is much more easily removed than in the case of hydrophobic poly-

ester fabrics. This difference in oil removal characteristics is apparently caused by a greater affinity of cotton fabrics for water. The differing hydrophilic/hydrophobic characteristics of cotton and polyester are due in part to the basic building blocks of the fibers themselves. That is, since polyester fibers are copolymers of terephthalic acid and ethylene glycol, they have less affinity for water because there are fewer free hydrophilic groups, e.g. hydroxyl or carboxyl groups, where hydrogen bonding can occur. With cotton, which is a cellulose material, the large number of hydrophilic groups provides compatibility with, and affinity for, water.

From a detergency standpoint, the most important difference between hydrophobic fabrics and hydrophilic fabrics is the tendency for oily soil to form easily removable droplets when present on a hydrophilic fabric and in contact with water. The mechanical action of washing and the action of synthetic detergents and builders normally used in the washing step of the laundering process removes such oil droplets from the fabric. This droplet formation is in contrast to the situation which exists with a polyester (hydrophobic) fiber. Water does not "wick" well through hydrophobic fabrics and the oily soil or stain tends to be retained throughout the fabric, both because of the inherent hydrophobic character of the fabric and the lack of affinity of oily soils for water.

Since polyester and polyester-blend fabrics (e.g. polyester-cotton blends) are susceptible to oily staining, and, once stained, are difficult to clean in an aqueous laundry bath, manufacturers of polyester fibers and fabrics have sought to increase the hydrophilic character of the polyester to provide ease of laundering.

A number of approaches to the problem of increasing the hydrophilic character of polyester fabrics and fabric blends have been taken. Many of these approaches involve a process employed by the textile/fiber manufacturer or the textile manufacturer. Netherlands Pub-

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lished Application 65/09456 [see also D. A. Garrett and P. N. Hartley, *J. Soc. Dyers and Colourists*, 82, 7, 252—7 (1967) and *Chem. Eng. News*, 44, 42—43 (October 17, 1966)] describes the treatment of polyester fabrics in which a copolymer of terephthalic acid with a polyethylene glycol is padded onto the polyester fiber using an emulsion containing a 20% concentration of the padding agent, a polyester swelling agent such as benzyl alcohol, and heat. The object of this treatment is to give the basic polyester fiber more hydrophilic character, thereby reducing the tendency of the polyester fiber to retain stains.

British Patent 1,088,984 relates to a modifying treatment for polyester fibers whereby a polyethylene terephthalate polymer is applied to the surface of said fibers. The polymers employed contain ethylene terephthalate and polyethylene oxide terephthalate units at a molar ratio from 1:1 to 8:1. The polyethylene oxide used for preparing these polymers has a molecular weight in the range of 300 to 6,000, preferably from 1,000 to 4,000.

British Patent 1,175,207 discloses a process for treating filaments and fibers by contacting same with polyesters containing from about 10% to about 50% by weight of crystalline polyester segments which are identical with the repeat units forming the crystalline segment of the polyester fiber, and from about 50% to about 90% by weight of water-soluble polyoxyalkylene ester segments. The polymers employed appear to be identical to those disclosed in British Patent 1,088,984.

British Patent 1,092,435 deals with a stable dispersion of water-insoluble graft polymers containing polyoxyethylene glycol and polyethylene terephthalate. These polymers have a ratio of ethylene terephthalate to polyoxyethylene terephthalate from about 2:1 to about 6:1. Also, the teaching of British Patent 1,119,367 relates to the application to fibers of surface modifying agents as described in the patents referred to hereinabove.

U.S. Patent 3,712,873, to Zenk, discloses the use of polyester polymers in combination with quaternary ammonium salts as fabric treatment compositions. Terpolymers having a molecular weight in the range from 1,000 to 100,000, and a molar ratio of terephthalic acid:polyglycol:glycol from 4.5:3.5:1 are disclosed. United States Patent Specification No. 3,893,929 relates to compositions and processes for imparting renewable soil release finish to polyester-containing fabrics. Polyesters based on terephthalic acid, ethylene glycol and polyethylene oxide, and their use in acidic fabric rinses, are disclosed. The polymers have a molecular weight in the range from 1,000 to 100,000, and the polyethylene oxide link has a molecular weight of 1300 to 1800.

DOS (German Offenlegungsschrift) 2,527,793 discloses compositions comprising nonionic surfactants, ethanolamine-neutralized

anionic surfactants, free ethanolamine and a soil-release polymer which can be identical to the polymers employed herein.

The prior art polymers do not provide an optimum solution to the soil release problem inherent with any hydrophobic fiber mainly because of lack of durability and marginal-to-unsatisfactory soil release performance. Moreover, many of the prior art soil release polymers lack the necessary substantivity to fibers under conditions of neutral-to-alkaline pH, i.e. under common laundering conditions. In addition, some of the known polymers seem to require calcium ions for fiber substantivity. Of course, the presence of free calcium or other water hardness cations is preferably avoided in a laundering operation.

It has now been found that certain hydrophilic terephthalate-based polymers having critical ratios of monomer units as well as critical limitations on the molecular weight of the hydrophilic moieties in the polymers are particularly useful as soil release agents. The in-use superiority of the polymers herein over those of the prior art is surprising in that nothing in the vast literature in this area suggests that the critical polymer design now provided would have any substantial effect on soil release properties. Moreover, the present compositions are provided in solid granular or powder form and are not limited to the liquid compositions DOS 2,527,793 mentioned above. This desirable result is made possible by using the polymers disclosed in U.S. Patent Specification No. 3,959,230, which describes terephthalate polymers composed of ethylene terephthalate and polyethylene oxide terephthalate. Such polymers are capable of imparting soil release properties to synthetic fibers in a dilute aqueous solution. These polymers are identical to those now found to be useful in granular or powdered detergent compositions.

The present invention provides particulate (which term includes "granular") detergent compositions capable of simultaneously cleaning and imparting improved soil release characteristics to fabrics, especially hydrophobic fabrics such as polyesters. The compositions herein comprise:

- (a) from 2% to 95% by weight of a detergent selected from water-soluble anionic, nonionic, zwitterionic and ampholytic surface-active agents and mixtures thereof; and
- (b) from 0.05% to 25% by weight of a soil release polymer comprising ethylene terephthalate units and polyethylene oxide terephthalate units at a molar ratio of ethylene terephthalate to polyethylene oxide terephthalate of from 25:75 to 35:65, said polyethylene oxide terephthalate units containing polyethylene oxide linking units having a molecular

weight of from 300 to 705, the overall molecular weight of the soil-release polymer being in the range of from 25,000 to 55,000.

5 The compositions herein can also contain various optional adjunct materials commonly employed in detergent compositions.

10 This invention enables the formulation of detergent compositions in particulate form that are capable of conferring effective soil release properties to fabrics. The chief advantage of such solid detergents over the liquid form is that substantial proportions of detergent builders can be conveniently used in solid compositions of the type disclosed herein.

20 The detergent compositions of the present invention comprise: (1) a surface-active agent; and (2) a specific type of polymer. These components are described in detail hereinafter. Unless stated to the contrary, the symbol "%" as used herein indicates percent by weight.

Surface-Active Component.

25 The surface-active agent is used in a detergent amount, i.e. an amount of from 2% to 95%, preferably from 5% to 30%, of the compositions herein. Since the soil release polymers herein are substantially electrically neutral polyesters, they are compatible with all manner of detergent surface-active agents. In fact, any of the well-known surface-active agents are useful herein. A list of typical surface-active detergents useful herein appears in U.S. Patent 3,719,647 and 3,707,504.

30 Examples of suitable surface-active agents useful herein include the group consisting of anionic, nonionic, ampholytic and zwitterionic detergents and mixtures thereof.

40 Preferred surfactants herein include the alkali metal alkyl benzene sulfonates in which the alkyl group contains from 9 to 20 carbon atoms in straight chain or branched-chain configuration, e.g., those of the type described in United States Patents Number 2,220,099 and 2,477,383 (especially valuable are linear straight chain alkyl benzene sulfonates in which the average of the alkyl groups is about 11.8 carbon atoms and commonly abbreviated as C_{11.8}LAS).

50 Another preferred surfactant type useful herein encompasses alkyl ether sulfates. These materials have the formula



55 wherein R is alkyl or alkenyl of 10 to 20 carbon atoms, x is 1 to 30, and M is a water-soluble cation such as alkali metal, ammonium and substituted ammonium. The alkyl ether sulfates useful in the present invention are sulfated condensation products of ethylene oxide and monohydric alcohols having 10 to

20 carbon atoms. Preferably, R has 14 to 18 carbon atoms. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from tallow are preferred herein. Such alcohols are reacted with 1 to 30, and especially 1 to 6, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific examples of alkyl ether sulfates useful herein are sodium coconut alkyl ethylene glycol ether sulfate; sodium tallow alkyl triethylene glycol ether sulfate; and sodium tallow alkyl hexaoxyethylene sulfate.

Other preferred surfactants herein are the olefin sulfonates having 12 to 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of α -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkane-sulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO₂ or chlorinated hydrocarbons when used in the liquid form, or by air, nitrogen or gaseous SO₂ when used in the gaseous form.

The α -olefins from which the olefin sulfonates are derived are mono-olefins having 12 to 24 carbon atoms, preferably 14 to 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene; 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1-tetra-

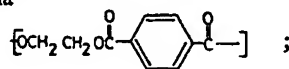
100 cosene. In addition to true alkene sulfonates and a portion of hydroxy-alkanesulfonates, olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, reactant ratios, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

Specific α -olefin sulfonates for use in the present invention are described more fully in U.S. Patent 3,332,880 of Phillip F. Pflaumer and Adriaan Kessler, issued July 25, 1967, entitled DETERGENT COMPOSITION.

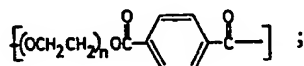
Soil Release Polymer.

115 The soil release polymers are used herein in an amount from 0.05% to 25%, preferably from 0.2% to 10%, and most preferably from 0.5% to 5%, by weight of the total compositions.

120 The soil release polymer component herein contains ethylene terephthalate units having the formula



and polyethylene oxide terephthalate units having the formula



the molar ratio of ethylene terephthalate to polyethylene oxide terephthalate being from 25:75 to 35:65, preferably about 30:70. In the formula, n is an integer from 7 to 16, i.e., the molecular weight of the polyethylene oxide linking unit is in the range from 300 to 705, preferably from 500 to 650. The polymers herein have a molecular weight in the range from 25,000 to 55,000, preferably from 40,000 to 55,000. The polymers are also characterized by a random structure, i.e., due to the method of preparation, any possible combination of ethylene terephthalate and polyethylene oxide terephthalate may be present.

The preferred polymers of this invention are prepared by using only those molar ratios of precursor materials which provide the critical ratios of ethylene terephthalate:polyethylene oxide terephthalate set forth above. These precursors are polymerized in the manner described hereinafter. For example, a highly preferred polymer herein is prepared from, and accordingly comprises, a mole ratio of terephthalic acid:ethylene glycol:polyethylene oxide of 1.0:0.3:0.7. Additionally, the preferred polymers of this invention have a melting point below 100°C.

The present polymers are substantive to hydrophobic fabrics, particularly polyester, under conditions of varying pH, particularly under the conditions of neutral to alkaline pH which occur during conventional fabric laundering operations. It is known that many prior art soil release polymers tend to become relatively less substantive to hydrophobic fabrics when applied under conditions of neutral-to-alkaline pH. Apparently, this pH substantivity relationship is due to the presence of free carboxylic acid groups in many of the prior art agents. Partial hydrolysis of such prior art materials seems to be a prerequisite to optimal performance. Moreover, the present polymers are substantive to fibers even under conditions involving low levels of calcium ions, such as obtain with built detergent systems. The deficiency of known polymers in this respect is related to the inefficiency in becoming affixed to polyester fibers in soft or low hardness water.

Polymer Preparation.

The polymerization process used herein is an esterification reaction similar to those known in the art. However, the concentrations and ratios of polymer precursors used in the process must be fixed so as to meet the compositional requirements of the present polymers.

More specifically, the polymers herein are prepared in the manner of U.S. Patent Specification No. 3,959,230 above. The polymers of this invention can be prepared according to the process described in the specification of British Patent 1,119,367, modified in the manner of U.S. Patent Specification No. 3,959,230, as follows.

194 g. dimethyl terephthalate, 67 g. ethylene glycol, 420 g. polyethylene oxide (molecular weight 600), 0.44 g. 2,6-di-tert-butyl-4-methylphenol, 0.0776 g. antimony trioxide, and 0.3024 g. calcium acetate are mixed in a suitable reaction vessel and heated to 210°C with stirring over a 1.5 hour period. During this time, methanol and some dimethyl terephthalate are distilled from the reaction vessel. The reaction temperature is then raised to 280°C and held there for two hours. Following addition of 0.282 g. of a 24.8% solution of phosphorous acid in ethylene glycol, a stream of nitrogen is blown over the reaction and allowed to exhaust for two hours. Dispersions of the polymer so formed are made by mixing the molten polymer with water in a Waring blender.

It should be noted that in the preparation of the preferred polymers herein the nitrogen exhaustion preferably lasts from 2 hours to 2.5 hours. Lowering the nitrogen exhaustion to 1.5 hours or increasing it to 3.0 hours adversely affects the soil-release characteristics of the polymers.

Optional Ingredients.

The compositions of the present invention desirably contain, as an optional ingredient, a water-soluble detergency builder component. Detergency builders are used at concentrations of up to 70%, preferably 20% to 70% by weight of the total detergent composition. As in the case of the surface-active agents, all manner of well-known detergency builders are compatible with the polymers herein and are suitable for use in the present detergent compositions. Such detergency builders serve to maintain the pH of laundry solutions containing the present compositions in the range of from 7 to 12, preferably from 8 to 11. Builders also enhance fabric cleaning performance and suspend particle soils released from the surface of the fabric.

Builders useful herein can be of the poly-valent inorganic and poly-valent organic types, or mixtures thereof. Non-limiting examples of suitable water-soluble, inorganic alkaline detergent builder salts include the alkali metal carbonates, borates, phosphates, polyphosphates, tripolyphosphates, bicarbonates, silicates and sulfates. Specific examples of such salts include the sodium and potassium tetraborates, perborates, bicarbonates, carbonates, tripolyphosphates, orthophosphates and hexametaphosphates.

Examples of suitable organic alkaline

detergency builder salts are (1) water-soluble amino polyacetates, e.g., sodium and potassium ethylenediamine tetraacetates, nitrilotriacetates and N - (2 - hydroxyethyl)nitrilotriacetates; (2) water-soluble salts of phytic acid, e.g., sodium and potassium phytates; (3) water-soluble polyphosphonates, including sodium, potassium and lithium salts of ethane-1-hydroxy-1,1-diphosphonic acid; and sodium, potassium and lithium salts of methylenediphosphonic acid.

Additional organic builder salts useful herein include the polycarboxylate materials described in U.S. Patent 2,264,103, including the water-soluble alkali metal salts of mellitic acid. The water-soluble salts of polycarboxylate polymers and copolymers such as are described in U.S. Patent 3,308,067 are also suitable herein. It is to be understood that while the alkali metal salts of the foregoing inorganic and organic poly-valent anionic builder salts are preferred for use herein from an economic standpoint, the ammonium, alkanolammonium, e.g., triethanolammonium and diethanolammonium, water-soluble salts of any of the foregoing builder anions are also useful herein.

Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is disclosed in Canadian Patent 755,038, e.g., a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate and trisodium ethane - 1 - hydroxy - 1,1 - diphosphonate.

While any of the foregoing alkaline poly-valent builder materials are useful herein, sodium tripolyphosphate, sodium nitrilotriacetate, sodium mellitate, sodium citrate, sodium oxydisuccinate and sodium carbonate are preferred herein for this builder use.

In addition to the ingredients described hereinbefore, the detergent compositions of this invention can also contain from 0.5% to 40% of other optional ingredients which make the product more effective and more attractive.

For example, organic and inorganic peroxy bleach compounds can be incorporated in the compositions in an amount from 5% to 40%.

The peroxy bleach compound can be represented by all usual inorganic and organic ingredients which are known to be satisfactory for use in detergent compositions. Examples of inorganic peroxy bleach compounds are the alkali metal perborates, percarbonates, persulfates, and perphosphates. As is well known, the perborates can have different degrees of hydration. Although frequently the tetrahydrate form is used, it is often desirable to employ the perborates having a lower degree of hydration, for example, one mole, two moles, or three moles of water. Organic peroxy bleach agents can be used as well. Sodium perborate is especially useful herein.

Specific examples of the organic peroxy-

bleach compounds are the water-soluble salts of mono- and di-peroxy acids such as perazelaic acid, monoperoxy-phthalic acid, diperoxy - terephthalic acid, 4 - chlorodiperoxy-phthalic acid. Preferred aromatic peracids include the water-soluble salts of diperisophthalic acid, m-chloroperbenzoic acid and p-nitroperbenzoic acid.

In the event the peroxy bleach compound is to be prepared *in situ*, then its precursors, i.e., a peroxy bleach agent and a peroxygen activator are added separately to the detergent composition. The peroxy bleach can be represented by all oxygen bleaching agents which are commonly used in detergent technology, i.e., organic and inorganic species, as mentioned hereinbefore. The activating agents can be represented by all oxygen activators known as being suitable for use in detergent technology. Specific examples of the preferred activators include acylated glycolurils, tetraacetyl methylene diamine, tetraacetyl ethylene diamine, triacetyl isocyanurate and benzoyl-imidazole. Acid anhydride activators which bear at least one double bond between carbon atoms α, α' to the carbonyl group of the anhydride radical can be used as well. Examples thereof are phthalic and maleic anhydrides. Especially preferred bleach activators are based on aldehydes, ketones, and bisulfite adducts of aldehydes and ketones. Examples of these especially preferred activators include: 1,4-cyclohexanedione; cyclohexanone; 3 - oxo - cyclohexylacetic acid; 4 - tertbutyl-cyclohexanone; 5 - diethylmethylammonio - 2-pentanone nitrate; N - methyl - morpholinoacetophenone nitrate; acetone; methyl ethyl ketone; 3 - pentanone; methyl - pyruvate; N-methyl - 4 - oxo - piperidine oxide; 1,4 - bis-(N - methyl - 4 - oxo - piperidinomethyl)-benzene chloride; N - methyltropinonium nitrate; 1 - methyl - 4 - oxo - tetrahydrothiopyranonium nitrate; N - benzyl - N-methyl - 4 - oxo - piperidinium nitrate; N,N-dimethyl - 4 - oxo - piperidinium nitrate; di-2-pyridylketone; and chloral hydrate.

In the event the per-bleach is prepared *in situ*, then the molar ratio of peroxygen bleach agent to bleach activator is preferably in the range from 5:1 to 1:2, especially from 2:1 to 1:1.2.

Other detergent composition ingredients used herein include suds regulating agents such as suds boosters and suds suppressing agents, tarnish inhibitors, soil suspending agents, buffering agents, brighteners, fluorescers, perfumes, dyes, inert carriers and mixtures thereof. The suds boosters can be the well-known diethanolamides. Silicones and hydrophobic alkylene oxide condensates can be used in the compositions for suds suppressing purposes or, more generally, for suds regulating purposes. Benzotriazole and ethylenethiourea can be used as tarnish inhibitors. Carboxymethyl cellulose is a well-known soil

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suspending agent. The above additional ingredients are employed in the usual concentration ranges, commonly 0.1% to about 1.5% of the total composition.

5 The detergent compositions of the present invention generally feel substantially dry, and can be prepared as dry powders, dry powder admixes or spray-dried granules in the manner well known in the detergency arts.

10 The following examples are illustrative of this invention, but are not intended to be limiting thereof.

EXAMPLE I.

15 A granular detergent composition useful for evaluating the in-use detergency performance of the polymers herein is as follows. The composition is typical of commercial, built detergents.

	Ingredients	Parts by Weight
20	Sodium linear dodecylbenzene sulfonate	7.5
	Sodium tallow alkylsulfate	9.2
	Condensation product of coconut alcohol with 6 moles of	
25	ethylene oxide	1
	Sodium tripolyphosphate	49.5
	Sodium silicate solids (ratio $\text{SiO}_2/\text{NaO} = 2.0$)	5.5
	Sodium sulfate	13.5
30	Moisture and minor ingredients	Balance to 100

The foregoing composition was used to evaluate the soil removal capabilities of the present polymers on hydrophobic textiles. The tests were of two types. In the first, the clean test fabric was laundered in an aqueous bath containing the above composition and either 50 ppm or 100 ppm of the soil release polymer being tested. In this "pre-wash" procedure, the polymer was established on the fabric surface prior to staining. In the second test, the fabric was stained prior to washing with the polymer-containing detergent. The "no pre-treatment" test results reflect the unexpectedly improved cleaning performance obtained with the polymers herein, whereas the "one pre-treatment" results demonstrate their superior soil release properties.

Desized 4 inch square polyester swatches, either pre-washed with the compositions of this invention or untreated, were soiled by spotting 0.01 ml. of various types of oily soils in the center of the swatch. The soiled swatches were allowed to wick for 18 hours at ambient conditions. Thereafter, soiled and reference swatches were laundered in an automatic miniature washer. Stain removal was determined gravimetrically by comparing the weight of the soiled swatch before and after laundering. Other testing parameters were: washing temperature—105°F; water hardness—7 grains/U.S. gallon; washing time—10 minutes; detergent concentration—0.12% by weight; and soil—as indicated.

TABLE I

Soil	One Pretreatment			
	Terpolymer			% Soil Removal
	PPM Polymer in Bath	Molar Ratio Ethylene Terephthalate to Polyethyleneoxide Terephthalate	Molecular Weight Polyethylene Oxide	
Crisco Oil*	0	Reference Swatch		17 (avg. 2 tests)
Crisco Oil	50	70:30	1540	61.5 (avg. 2 tests)
Crisco Oil	50	30:70	600	85 (avg. 2 tests)
Bacon Grease	0	Reference Swatch		28
Bacon Grease	100	30:70	600	49
Bacon Grease	50	30:70	600	61
Crisco Oil	0	Reference Swatch		17
Crisco Oil	100	30:70	600	83
Dirty Motor Oil	0	Reference Swatch		27
Dirty Motor Oil	100	70:30	1540	10
Dirty Motor Oil	100	30:70	600	78
		No Pretreatment		
Crisco Oil	0	Reference Swatch		17
Crisco Oil	100	70:30	1540	40
Crisco Oil	100	30:70	600	69

* "Crisco" is a trade mark.

The foregoing clearly demonstrates that the polymers of the present invention provide superior soil release properties over superficially similar prior art polymers formulated with opposite ratios of ethylene terephthalate and polyethylene oxide terephthalate, using high molecular weight polyethylene oxide. The test results also demonstrate the improved cleaning performance of the compositions herein.

A granular detergent composition was prepared having the following formula:

EXAMPLE II.

15	<u>Ingredients.</u>	<u>Parts by Weight</u>
	Sodium linear dodecylbenzene sulfonate	14.5
	Sodium tripolyphosphate	49.6
20	Sodium silicate solids (ratio SiO ₂ /Na ₂ O = 2)	5.9
	Sodium sulfate	14.9
	Moisture and minor ingredients	Balance to 100

The above composition was used to evaluate the soil release properties and cleaning performance of the polymers herein by a visual grading technique. Visual grades were assigned to polyester test swatches using a grading scale from 0 to 5, whereby 0 represents no removal and 5 represents complete removal. The results shown represent the average rat-

ings of, at least, two expert judges.

In the tests the swatches were prewashed prior to soiling in an aqueous solution of the above composition and 250 ppm of the soil release polymer. The washing temperature was 125°F and the water hardness was 7 grains/U.S. gallon. Results are set forth in Table II.

TABLE II

Soil	Terpolymer			Score
	PPM Polymer in Bath	Molar Ratio Ethylene Terephthalate to Polyethyleneoxide Terephthalate	Molecular Weight Polyethylene Oxide	
Dirty Motor Oil	0	Reference Swatch		0
Dirty Motor Oil	250	30:70	600	5
Bacon Grease	0	Reference Swatch		2.6
Bacon Grease	250	30:70	600	5
Mineral Oil	0	Reference Swatch		2.2
Mineral Oil	250	30:70	600	5
Margarine	0	Reference Swatch		2.3
Margarine	250	30:70	600	5

In the foregoing tests, comparable soil release and cleaning performance are also obtained when the polymer (molar ratio ethylene terephthalate to polyethylene oxide terephthalate 30:70; MW polyethylene oxide 600) is successively replaced by polymers having molar ratios of ethylene terephthalate to polyethylene oxide terephthalate of 25:75; 28:72; 31:69; and 35:65, respectively, wherein the polyethylene oxide linking unit in the polyethylene oxide terephthalate has a molecular weight of 500; 530; 560; 580; 600; 620; and 650, respectively.

Substantially comparable results are also secured when the sodium linear dodecyl benzene sulfonate in the foregoing composition is replaced by the other surface-active materials set forth hereinabove, respectively.

WHAT WE CLAIM IS:—

1. A particulate detergent composition having soil release properties comprising:

(a) from 2% to 95% by weight of a detergent selected from water-soluble anionic, nonionic, zwitterionic and ampholytic surface-active agents and mixtures thereof; and

(b) from 0.05% to 25% by weight of a soil release polymer comprising ethylene terephthalate units and polyethylene oxide terephthalate units at a molar ratio of ethylene terephthalate to polyethylene oxide terephthalate of from 25:75 to 35:65, said polyethylene oxide terephthalate units containing polyethylene oxide linking units having a molecular weight of from 300 to 705, the molecular weight of said soil-release polymer being in the range of from 25,000 to 55,000.

2. A composition according to claim 1, wherein the surface-active agent is present in an amount from 5% to 30% by weight.

3. A composition according to claim 1 or 2 wherein the soil release polymer is present in an amount from 0.2% to 10% by weight.

4. A composition according to claim 1, 2 or 3, wherein the soil release polymer has a molecular weight in the range from 40,000 to 55,000.

5. A composition according to any of claims 1 to 4, wherein the soil release polymer contains polyethylene oxide linking units having a molecular weight in the range from 500 to 650.

6. A composition according to any of claims 1 to 5, wherein the soil release polymer contains ethylene terephthalate and polyethylene oxide terephthalate units in a molar ratio of about 30:70.
7. A composition according to any of claims 1 to 6, wherein the surface-active agent is selected from:
- (i) olefin sulfonates having from 12 to 24 carbon atoms in the molecule;
 - (ii) alkylether sulfates of the general formula $RO(C_2H_4O)_xSO_3M$ wherein R is alkyl or alkenyl of 10 to 20 carbon atoms, x is an integer from 1 to 30, and M is a water-soluble cation; and
 - (iii) alkali metal alkyl benzene sulfonates having from 9 to 20 carbon atoms in the alkyl group.
8. A detergent composition according to any of claims 1 to 7 which also comprises from 20% to 70% by weight of a detergency builder.
9. A composition according to claim 1 substantially as hereinbefore described and/or exemplified.
- For the Applicants,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
43, Bloomsbury Square,
London, W.C.1.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1977.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

